CO_2 Removal By Using Silica Based Membrane

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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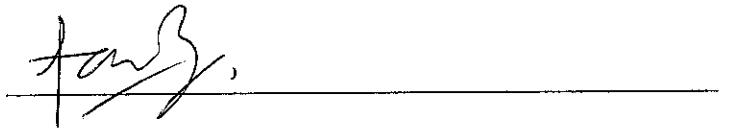
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

June 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



FARHANA BINTI KAMARUDIN

ABSTRACT

Practically in industry use amine adsorption as an absorbent for removing carbon dioxide which is categorized under acidic gas group. However the cost of acid gases removal by using the mixed amines system is highly expensive. One way to reduce the cost of amine is by replacing amine adsorption with other method which is more economical and easy to optimize called membrane technology.

This porous silica membrane layer provides the stability and allows a free flow of the compounds that permeate through the selective layer. They can operate at elevated temperatures, with many ceramic membranes usable at over 1000°C. They are also much more resistant to chemical attack, have excellent thermal stability and resistance to corrosive liquids and gases. Inorganic membranes compete with organic membranes for commercial used. In many of the harsh operational environments listed above, organic membranes will not perform well, or will not survive at all. For these environments, only inorganic membranes offer needed solutions.

This research project consists of two experiments; preparation of α-Alumina Substrate and Preparation of silica Membrane using sol-gel method. For the first experiment the goal is to achieve 20-25% porosity of the substrate. For the second experiment, nitric acid is used as a catalyst for silica sol preparation because of its low branched cluster that will result a narrower pore size of the porosity substrate. The effect of dipping time (1,2 and 3 hours) during dip-coating of the porous alumina support also been studied and it resulted the silica membranes with 3 hours dipping time gives highest CO_2 permeance.

ACKNOWLEDGEMENTS

Alhamdulillah, thanks to Allah SWT, whom with His willing giving me the opportunity to complete this Final Year Project entitle Carbon Dioxide Removal Using Silica Based Membrane.

Firstly, I would like to express my deepest thanks to, Dr. Azmi bin Bustam, a lecturer of Chemical Engineering Department at UTP and also assign, as my supervisor who had advice and guided me a lot during two semesters session 2009/2010. He inspired me greatly to work in this project. His willingness to motivate me contributed tremendously to my project.

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CHAPTER 1
PROJECT BACKGROUND

1.1 Background of Study

Carbon dioxide, which falls into the category of acid gases is commonly found in natural gas streams at levels as high as 80% in combination with water, it is highly corrosive and rapidly damages pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity.[1]

Moreover, the excessive discharge of CO_2 into the atmosphere due to the consumption of large amounts of fossil fuels has become one of the most serious global environment problems. The increase of CO_2 concentration in the atmosphere is considered to be the major cause for global warming.[3]

CO_2 separation and collection processes consist of absorption, adsorption, membrane separation and the other separation processes such as cryogenic.CO_2 separation by absorption into a reactive solvent such as monoethanol-amine (MEA) is considered to be prohibitively expensive. The cryogenic separation of CO_2 consumes considerable energy due to heating and cooling. Membrane separation of CO_2 offers in situ separation without changing the ambient temperature.[3]

1.2 Problem Statement

1.2.1 Problem Identification

The pipeline transportation specification states that sales gas is to contain less than 2% CO_2. But the ultimate goal is to develop the most efficient and cost-effective separation unit have to take into considerations. For those matters, there are two methods used in the industry in removing CO_2 from natural gas stream, which are amine adsorption plant and membrane (polymeric or ceramic membrane). Due to those constraint offered by amine plant and polymeric membrane, a microporous inorganic ceramic membrane are used.

Besides having well-known thermal and chemically stability, ceramic membranes usually have a much higher gas flux as compared with polymeric membranes. Ideally one would like to have both high flux and high specific selectivity for the gas interest. In general, high selectivity can be achieved when the membranes can be made to have a pore size less than 2nm in diameter. In order to produce ceramic materials possessing this type of pore size, the sol-gel technique has often been employed.[2]

1.3 Objective and Scope of Study

The objectives of the project are:

i. To fabricate porous alumina membrane support with porosity between 20%-25%
ii. To coat thin layer membrane silica sol on top of fabricated alumina
iii. To evaluate permeability of carbon dioxide and methane on the fabricated alumina membrane

The scope of study for this research project are :

- To do the literature review of membrane separation technique – CO_2/CH_4 gas stream
- To apply appropriate methodology in conducting the experiment to produce good results and findings-Temperature and Pressure

1.4 Feasibility of the Project

Chemical engineering students need to complete the project within 2 semesters. It is presume that the project is feasible within the scope and time frame if there are no issues with regard to equipment function and material availability. Research work is allocated to be done in first semester while the experimental work has been started in this semester.

CHAPTER 2
LITERATURE REVIEW

2.1 Membranes

A membrane acts as a semi-permeable barrier. The CO_2 passes through this barrier more easily than other gases. In general, the rate at which a particular gas will move through the membrane can be determined by the size of the molecule, the concentration of gas, the pressure difference across the membrane and the affinity of the gas for the membrane material.

Membranes, made of polymers or ceramics, can be used to effectively sieve out carbon dioxide from gas streams. The membrane material is specifically designed to preferentially separate the molecules in the mixture. A range of configurations exists either simply as gas separation devices or incorporating liquid absorption stages. This process has not yet been applied on a large scale and there are challenges related to the composition and temperature of the flue gases

Membranes are used to separate CO_2 from other gases (gas separation membranes) and to allow CO_2 to be absorbed from a gas stream into a solvent (membrane gas absorption). Other membranes being developed are facilitated transport membranes. There are a range of membranes types for these processes.

2.2 Theory of gas separation

The performance of a gas separation membrane system is largely determined by three parameters. The first parameter is its permselectivity or selectivity towards the gases to be separated. Permselectivity affects the percentage recovery of the valuable gas in the feed. The second issue is the permeate flux or permeability which is related to productivity and determines the membrane area required. The third parameter is related to the membrane stability or service life which has a strong impact on the replacement and maintenance cost of the system.

A frequently used indicator of how much of two gases in a multicomponent gaseous mixture are separated with respect to each other through a membrane is called the separation factor. It is defined as

$$\alpha_{m,n} = \frac{y_m / x_m}{y_n / x_n}$$

where y and x represent the mole fractions of the gas components feed side and permeate side of the membrane, respectively. It is essentially determined by their relative.[3]

2.3 Mechanisms of gas separation

The advantage of using gas separation membranes is that the equipment is much smaller and there is no solvent involved. At the current stage of development, the main cost is the energy required to create a large enough pressure difference across the membrane to drive separation.

There are a number of mechanisms for gas separation in membranes:

1. **Knudsen diffusion**: gas components are separated based on the difference in the mean path of the gas molecules.

2. **Molecular sieving**: gas components are separated based on size exclusion, the size being the kinetic diameter of the gas molecules.

3. **Solution-diffusion**: the gases are separated by their solubility within the membrane and their diffusions through the dense membrane matrix. This is the usual separation mechanism for polymeric membranes (rubbers, polyimide, cellulose acetate).

4. **Surface diffusion**: gas molecules with higher polarity are selectively adsorbed onto the surface of the membrane and pass through the membrane by moving from one adsorption site to another (see adsorption).

5. **Capillary condensation** :The most common are molecular sieving and solution-diffusion.

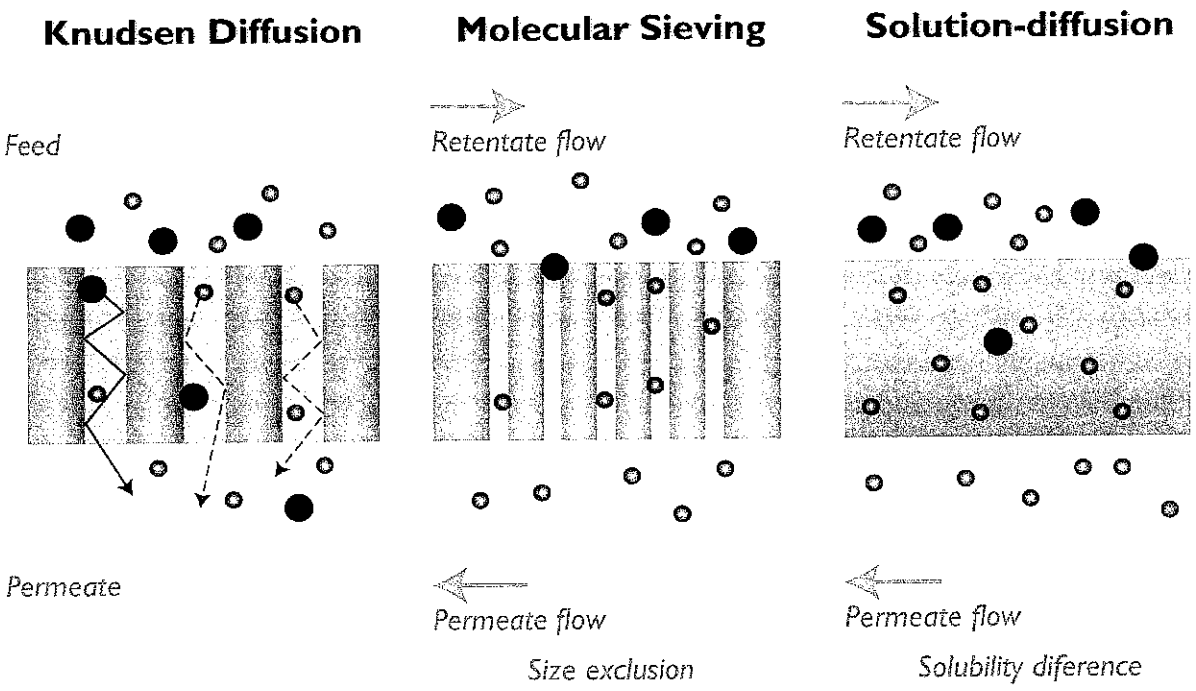


Figure 2.1 : Schematic representation of three of the different possible mechanisms for membrane gas separation (after Scholes, Kentish and Stevens).

2.3.1 Knudsen Diffusion

Knudsen mode of gas transport is important when the mean free path of the gas molecules is much greater than the pore size of the membrane [11]. In such situation the collisions of the molecules with the pore wall are more frequent than the collisions among molecules. This mechanism is often predominant in macroporous and mesoporous membrane [12] and described by Knudsen Equation for diffusive flow of molecules in a capillary tube in this regime.

2.3.2 Derivation of Transport Equation

Consider a gas with a molecular density of n (molecules/m^3) at one side of a hole and a vacuum at the other side. The free-molecule flux J_K (molecules/m^2) through the hole is given by:

$$J_K = w n \bar{C} \qquad (1)$$

Where, w is a dimensionless probability factor, and C is the mean molecular speed (m/s).

If there is gas on both sides of the hole, the net flux is proportional to the difference in gas number densities at the two sides:

$$J_K = w \bar{C}(n_2 - n_1) \qquad (2)$$

In order to use this equation, expressions are required for the mean molecular speed and the dimensionless probability factor. The mean molecular speed is readily calculated using kinetic theory (derivation to follow) as:

$$\bar{C} = \sqrt{\frac{(8RT)}{\pi \cdot M}} \qquad (3)$$

Where, R is the universal gas constant (J/kmol K), T the temperature (K), and M the molar mass of the gas (kg/kmol). Calculation of the probability factor is considerably more complicated, requiring knowledge of the hole geometry and the appropriate scattering law. Values of w for two simple geometries with the assumption of diffuse scattering, to which many physical situations can be approximated are: (1) an infinitesimally thin orifice for which w= ¼; and (2) a long straight circular tube of radius r and length L (L>>r) for which the value of w is given by (2/3)(r/L). The method of derivation of these expressions is presented in [3].

The widely used Parallel Pore model of porous media uses the later of the above simple geometries. Development of this model is as follows. Substituting w=(2/3)(r/L) and C as given by equation (3) gives:

$$J_K = \left(\frac{2r}{3L}\right)\sqrt{\frac{(8RT)}{\pi \cdot M}}(n_2 - n_1) \qquad (4)$$

Which can be re-written in differential form (applied along the axis of the cylindrical pore) and applying the convention that flux moves from high to low concentration as:

$$J_K = -\left(\frac{2}{3}r\right)\sqrt{\frac{(8RT)}{\pi \cdot M}}\left(\frac{dn}{dz}\right) \qquad (5)$$

Considering the flux ***JK*** to be in mol not molecules, and considering the rate of change of gas concentration (mol/m3) rather than molecular concentration gives:

$$J_K = -\left(\frac{2}{3}r\right)\sqrt{\frac{(8RT)}{\pi \cdot M}}\left(\frac{dc}{dz}\right) \qquad (6)$$

Hence, by analogy to continuum gas diffusion, we can now define a Knudsen diffusion coefficient ***DK*** for flow in a long straight pore with diffuse scattering as:

$$D_K = \frac{2}{3}r\sqrt{\frac{(8RT)}{\pi \cdot M}} \qquad (7)$$

Hence, the Knudsen diffusion coefficient is proportional to the pore radius and the mean molecular velocity.

2.3.3 Knudsen Coefficient

The formula given for Knudsen flow in equation (6) is specific to cylindrical passages. Analyzing different geometries yields equations of the same form but with different geometrical parameters and for this reason a general equation is often defined using a Knudsen Coefficient ***Ko*** (c.f. viscous flow parameter).

This parameter, which relates the theory of free-molecule flow to a specific physical application, has the value of the dimensionless probability factor ***w*** multiplied by a constant coefficient of 4/3 (which I assume has some historical origin). It is **not** the same as the Knudsen Diffusion Coefficient ***DK***.

The Knudsen Coefficient is the *defined* through:

$$D_K = \frac{4}{3} K_0 \bar{C} \qquad (8)$$

2.4 Membrane structure – Selective layer

Membrane can be classified into three; **porous membranes** classify according to size particles or molecules, **non-porous membranes** classify according to chemical affinities between components and membrane materials and also **carrier membrane** classify according to carrier transport.[9]

In porous membranes the selectivity is mainly decided due to the size of the pores. These types of membranes are used in microfiltration and in ultrafiltration. As stated by Hartmut Bruschk (1995) a gradient in hydraulic pressure acts as the driving force. Small molecules of the solvent of a solution, usually water, can pass through the pores, whereas particles or large molecules are retained.

The non-porous membranes are normally used in gas separation and pervaporation. In these membranes the molecules first dissolves into the membrane and then diffuse through it. The separation is based on how well different compounds dissolve and diffuse through the membrane. Some molecules diffuse fast and others diffuse slowly. Example of non-porous membrane is polymeric membrane such as polysulfone and polycarbonate.

In the carrier transport membranes a specific carrier molecule facilitates the transport of a specific molecule through the membrane. This kind of transport occurs for example in the lipid bilayer of a cell. The carrier mediated transport is very selective and can be used to remove components like gases, liquids, and ironic or non-ironic components

2.5 Typical membrane structure for gas separation

Membrane materials are usually made as thin as possible to increase the permeability, which is the ability of a chemical to pass through a material. This makes the membrane very fragile.

To overcome this problem the membranes are made with an asymmetric structure where the thin selective nonporous layer is grafted on a thicker porous layer of the same material[10]. This porous layer provides the stability and allows a free flow of the compounds that permeate through the selective layer. The disadvantage of this membrane structure is that as they are made of only one type of material, which is normally very expensive. This problem is solved by making a composite membrane. This consists of a thin selective layer made from one type of polymer, which is on top of another asymmetric membrane composed of another polymer.

These types of composite membranes are being used in most of the newer advanced CO_2 removal membranes as the selective layer can be adjusted without increasing the membrane cost too much.

2.5.1 Organic Membrane

The most commonly used membrane materials. There are large numbers of polymer materials available. Some of the advantages of polymers are flexibility, permeability and ability to be formed into a variety structures. On the other hand, polymers are generally not thermally stable, which can be a problem for many separation tasks. The polymer morphology and mobility determine the gas permeability and selectivity.

2.5.2 Inorganic Membrane

Inorganic membranes are versatile. They can operate at elevated temperatures, with metal membranes stable at temperatures ranging from 500-800°C and with many ceramic membranes usable at over 1000°C. They are also much more resistant to chemical attack. Because of the wide variety of materials that may be used in the fabrication of our inorganic membranes, resistance to corrosive liquids and gases, even

at elevated temperatures can be realized. Inorganic membranes compete with organic membranes for commercial used. In many of the harsh operational environments listed above, organic membranes will not perform well, or will not survive at all. For these environments, only inorganic membranes offer needed solutions.

In this project the focus is only for inorganic membrane because of its physical properties and become demand for the time being.

2.6 Ceramic membrane for gas separation

Ceramic membranes are made from inorganic materials (such as alumina, titania, zirconia oxides or some glassy materials) and they are used in membrane operations. By contrast with polymeric membranes they can used in separations where aggressive media (acids, strong solvents) are present. They also have excellent thermal stability which makes them usable in high temperature membrane operations.

Like polymeric membranes they are either dense or porous. Dense Ceramic Membranes are made from crystalline ceramic materials such as fluorites, which allow permeation of only oxygen or hydrogen through the crystal lattice. Therefore, they are most impermeable to all other gases, giving extremely high selectivity towards oxygen or hydrogen. They are mainly composed of amorphous silica or zeolites. They are usually prepared as a thin film supported on a macroporous ceramic support, which provides mechanical strength, but offers minimal gas transfer resistances. In most cases, some intermediate layers are required between the macroporous support and the top separation layer to bridge the gap between the large pores of the support and the small pores of the top separation layer.

Given their unique mechanical strength, thermal stability and organic solvent resistance, ceramic membranes offer excellent potential for gas separations in process industries where operating conditions are rather severe. In recent years, technological improvements have made it possible to manufacture microporous membranes free of defects. However, a poor understanding of the mechanism of their operation, and a lack of reliable data on their performance have significantly limited large scale applications

of these membranes, and may have inhibited their further commercial development. The interest in improving this situation is evidenced by the amount of very recent research that concerns the transport of binary and multicomponent hydrocarbon mixtures through inorganic membranes. Systems studied have included nitrogen–methanol–ethanol through alumina, C_1–C_4 alkanes and alkenes, carbon dioxide, hydrogen and iso-octane through silicalite-1, C_1–C_4 alkanes through silicalite-1, C_1–C_{10} normal alkanes through silicalite, C_2 and C_3 alkenes through silicalite-1, and butane isomers through zeolite MFI.

2.7 Sol-gel Method

Sol-gel methods for preparing silica membranes can be generally divided into two groups: polymeric and particulate. In polymeric sol-gel methods, there are chainlike macromolecules in the sol. This makes it easier to form coatings without cracks. Silica membranes that have a thickness less than 1μm, and have pore size in the micropore range were reported to be produced by this technique. However, the pore size distribution and pore volume in these polymeric silica membranes can not be easily controlled. Furthermore, the gas flow through these membranes is typically low. In contrast, the sol-gel method involving particles uses colloidal suspensions of silica particle precursors. Silica gels having uniformly distributed pore size and large pore volume were obtained from this method. Unfortunately, the biggest difficulty of using sol-gel methods involving particles is that cracks in the coatings are hard to avoid during drying. These cracks are driven by the tensile stress generated when the pore liquid evaporates. In many cases, the coating process is the key step in this membrane preparation method.

Slip-casting is the most frequently used technique in the coating of colloidal sols onto porous substrates. The film containing particles is formed on a porous support by passing the solution through the support and leaving the particles on the support surface. This process is driven by capillary force. When the support is too thin, capillary force is not sufficient and slip-casting is not effective. Uniform alumina membranes on hollow

fiber supports were fabricated using this method. Cracks and pinholes were avoided. In this manner, homogeneous thin coatings can be produced.

The silica sol used in this project was prepared by a sol-gel method that yielded particle sols. Membranes produced by the filtration method were of better quality than those prepared by slip-casting.[2]

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

There are two major components in this silica membrane which are Porous Alumina support that used as a support substrate for silica sol (silica membrane) and silica sol-gel itself. Therefore, there will be two stages of membrane synthesis which are:

i. Preparation of porous Alumina Membrane Support
ii. Synthesis of the coating gel (silica sol)

3.1.1 Synthesis of Porous Alumina Support

Porous alumina, α-Al_2O_3 supports are made from alumina powder. The supports are pressed at 6 tonnes, and sintering at 1500°C for 3 hours. The final porosity should be in range of 20-25% determined using method base on the displacement of water into the substrate.

Experimental : Preparation of porous alumina support using extrusion method

The materials used for the support are aluminium oxide powder, starch and distilled water. Starch is used as a binder in developing porous alumina substrate.

Methodology :

1. Firstly, 100 ml beaker is filled with distilled water and boiled till it reached 100°C.
2. Weighted 10 g of starch and dissolved it in the boiled water by using spatula.
3. The starch solution is cooled to the room temperature.
4. Then,10 g of aluminium oxide and is prepared on the glass plate.
5. By using a dropper,10 drops of starch solutions is used on the aluminium oxide powder.

6. Then, grind it together in the mortar for few minutes until it mixed well.
7. The powder is poured in the die press and pressed it using hand press at the pressure of 6 tonnes.
8. Steps 4 to 7 are repeated until we get a perfect alumina discs.
9. Then, the alumina discs were sintered at temperature 1300°C in the furnace for 3 to 4 hours.

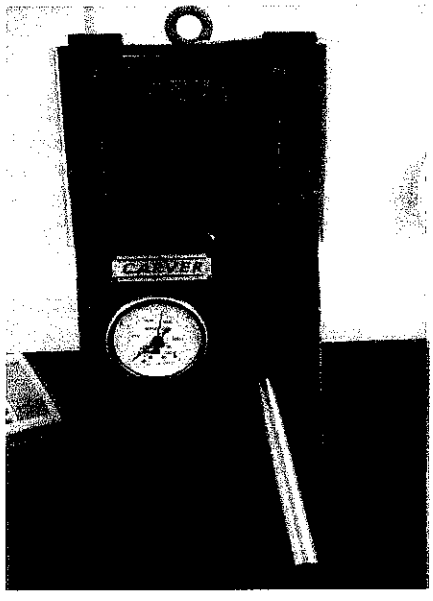


Figure 3.1 : Hand Press

Porosity calculation of α-Alumina Substrate

1. The reading of the weight of alumina substrate on air is taken.
2. The reading of the weight of alumina substrate in water is taken.
3. The reading of the weight of alumina substrate after it was immersed in boiled water for an hour is taken.

$$\% \text{ porosity} = \frac{\text{Weight in boiling water for 1 hr} - \text{weight in air}}{\text{Weight in boiling water for 1 hr- weight in water}} \times 100\%$$

3.1.2 Synthesis of Silica Sol-gel

1. The solution of silica sol was prepared by dissolving 10.63 ml tetraethyl orthosilicate (TEOS), 53.15 ml ethanol, 100 ml distilled water and 0.5ml nitric acid as a catalyst
2. Mix all the chemicals in a glass bottle. Stir the mixture vigorously.
3. The solution is left for 48 hours before dip coating method.

Sol-gel silica is prepared by base catalysis of tetraethyl orthosilicate,TEOS (Aldrich) and distilled water, with ethanol used as a solvent. As catalyst, nitric acid (HNO_3) are used. Silica membranes are prepared by dip-coating a prepared porous alumina support in a polymeric silica sol made by base-catalyzed hydrolysis and condensation of TEOS, $Si(OCH_2CH_3)_4$, in ethanol. The support are dipped in the sol in a vertical position, maintained submerged for an hour, 2 hours and 3 hours. After withdrawal, the membranes are dried inside the oven and after drying, they are calcined in the furnace for 3 hours at 500°C.

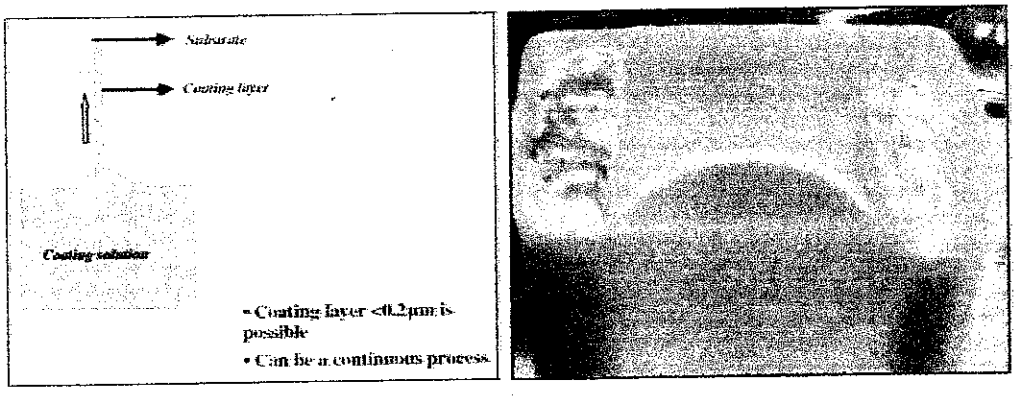


Figure 3.2 : Dip-coating method of the porous alumina support in silica sol

3.1.3 Membrane Characterization Techniques

i. Scanning Electron Microscope (SEM)

ii. Gas Permeation Test

The morphology/structure and thickness of the silica membranes were determined by SEM. The SEM pictures were taken after the membranes were calcined. While for gas permeation test, we will get the result of permeation related parameter.

3.1.3.1 Scanning Electron Microscope (SEM)

The SEM is a microscope that uses electrons instead of light to form an image. The scanning electron microscope has many advantages over traditional microscopes. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time. The SEM also has much higher resolution, so closely spaced specimens can be magnified at much higher levels. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today.

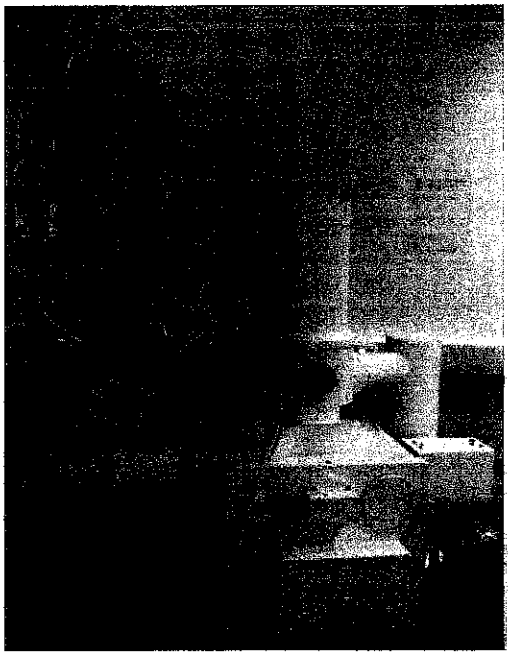


Figure 3.3 : Scanning Electron Microscope (SEM)

3.1.3.2 Gas Permeation Test

Gas permeation measurements were performed using pure CO_2 and pure CH_4. The permeation experiments flow single gas component of CO_2 and CH_4 through membrane disc. The equipment is used to carry out the gas permeation measurement. The set-up consists of a feed gas tank, a pressure gauge of inlet gas, a dead-end membrane cell and a bubble soap flow meter. Membranes are located in the dead-end membrane cell or module. This type of module allows the feed gas to flow into the membrane perpendicularly to the membrane position [8].Feed side pressure were varied from 2 bar to 3.5 bar.

Before starting the experiment, the gas permeation test unit was evacuated to less than 0.1 bar by vacuum pump for an hour to remove all residual gases remaining in the equipment. The feed gas was supplied directly from the gas tank, which is equipped with a pressure regulator. The feed gas was supplied directly from the gas tank, which is equipped with a pressure regulator. The feed gas pressure was set up within range of test pressure and the permeate stream was assumed to be at atmospheric pressure. In this permeation experiment, time (t) required to reach certain volume of gas in the permeate stream was observed and recorded. In addition, the volume of gas (V) in permeate stream was also measured using a bubble soap flow meter. The permeation of each gas through a membrane was measured twice at steady state condition.

Based on the volumetric measurements of the permeated gas, the volumetric flow rate Q, was calculated as follows:

$$Q = \frac{V}{t} \tag{3.1}$$

This volumetric flow rate was then corrected to STP conditions (0°C and 1 atm) using the following equation:

$$Q_{STP} = \frac{T_{STP} \times Q}{T} \quad (3.2)$$

In which TSTP and QSTP referred to temperature (K) and volumetric of permeate gas (cm3/s) at STP condition. After conversion into STP condition, gas permeance, P was then calculated using the following formula

$$P = \frac{Nt}{A\Delta p} \quad (3.3)$$

Where Δp and A were trans-membrane pressure and effective membrane area, respectively. Nt is the gas permeation rate (mol/s) and can be calculated as follows :

$$Nt = \frac{Q_{STP} \times \rho_{CO2}}{M_{CO2}} \quad (3.4)$$

Where ρ_{CO2} and M_{CO2} were CO_2 density and molecular weight of CO_2, respectively. The CO_2/CH_4 ideal selectivity (unitless), $\alpha_{CO2/CH4}$, of membrane can be determined by dividing CO_2 permeance, $(P)_{CO2}$, over CH_4 permeance, $(P)_{CH4}$

$$\alpha_{CO2/CH4} = \frac{(P)_{CO2}}{(P)_{CH4}} \quad (3.5)$$

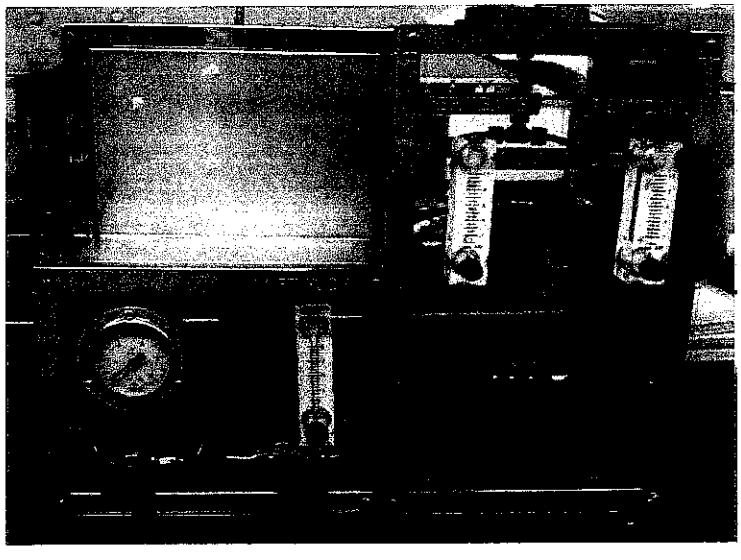
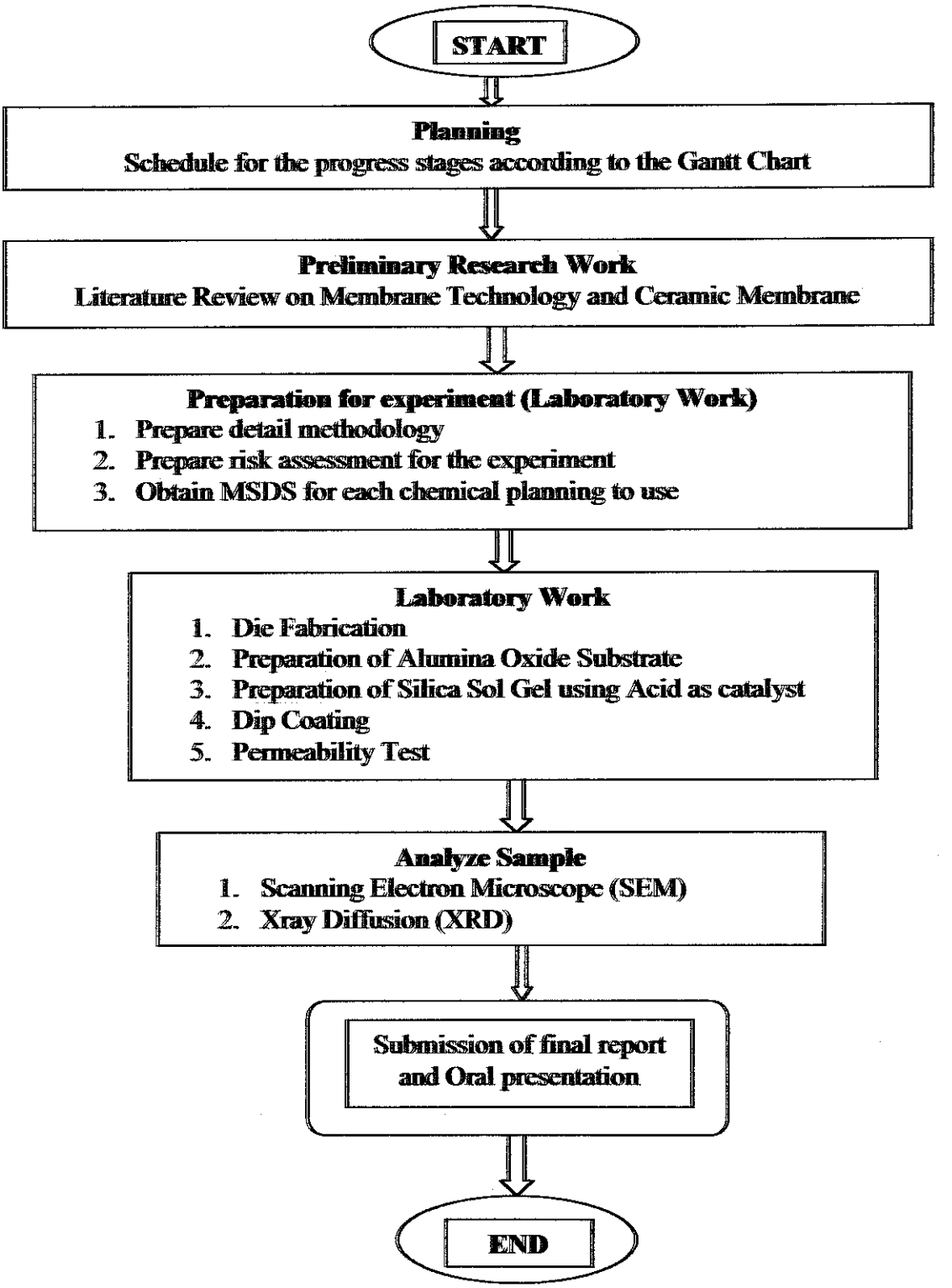


Figure 3.4 : Gas Permeation Test

3.2 Project activities



3.3 Key milestone and Gantt Chart

Suggested Milestone for the First Semester of 2-Semester Final Year Project

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■											
3	Submission of Preliminary Report				●											
4	Seminar 1 (optional)					■	■	■								
5	Project Work					■	■	■								
6	Submission of Progress Report									●						
7	Seminar 2 (compulsory)										■	■	■	■		
8	Project work continues									■	■	■	■	■		
9	Submission of Interim Report Final Draft														●	●
10	Oral Presentation		●													

Mid-semester break

● Suggested milestone

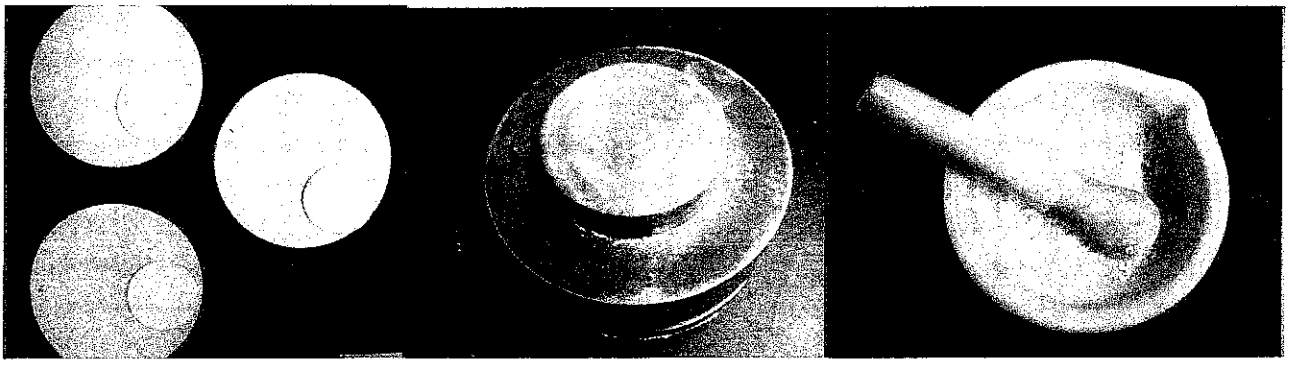
■ Process

3.4 Tools Required

In this project, tools required for the experiment such as furnace, oven, gas permeation test, die and hand pressing, and Scanning Electron Microscopy (SEM). Furnace is used to sinter the alumina discs at temperature to 1500°C. There are several common type of furnaces; electric-arc furnaces, induction furnaces, crucible furnaces and cupolas. Oven at temperature 100°C is used to dry the membranes. Extrusion die and hand press used in extrusion of alumina powder to form porous alumina discs.

CHAPTER 4

RESULT AND DISCUSSION



(a) (b) (c)

Figure 4.1: (a) The porous alumina support before sintering process (b) Die press (c) Mortar and Pestle

4.1 Porosity calculation of α-Alumina Substrate

Table 4.1 : Calculation for porosity calculation of α-Alumina Substrate

Sample	Weight in air	Diameter	Weight in water	Weight in boiling water for 1hr	Porosity %
1	9.913 g	2.5 cm	4.252 g	11.427 g	21.1
2	9.854 g	2.5 cm	4.120 g	11.406 g	21. 3
3	9.927 g	2.5 cm	4.288 g	11.426 g	21.0

$$\% \text{ porosity} = \frac{\text{Weight in boiling water for 1hr} - \text{Weight in air}}{\text{Weight in boiling water for 1hr-Weight in water}} \times 100\%$$

$$\text{Bulk Porosity} = \frac{(11.427-9.913)}{(11.427-4.252)} \times 100\% = 21.1\%$$

From the 3 samples, the average porosity of the alumina discs are 21%.

4.2 Morphological characterization of silica membrane

Surface morphology and cross-sections of membranes were studied by SEM. Figure 4.2 (a), (c), and (e) show the top view of the silica membrane with different dipping time of an hour, 2 hours, and 3 hours. These figures indicate the discrete layer of silica is successfully formed on top of porous alumina support. While Figure 4.2 (b), (d), and (f) show the cross-section view of the silica membranes which indicate clearly the silica layer deposited on top of the porous alumina support layer as a distinct separation between the two layers present.

Indeed, the skin layer was formed successfully. From the SEM observation, the surface of the support was covered with a continuous layer of silica particles and its grown within the pores of the support. The silica membrane was tightly attached to the substrate and the thickness of the membrane varies from 8-15μm. From these figure it shows that the thickness of silica membrane is proportional to the dipping time.

This method has been shown to be very effective for the formation of mesoporous silica membranes on a support with relatively large pores.

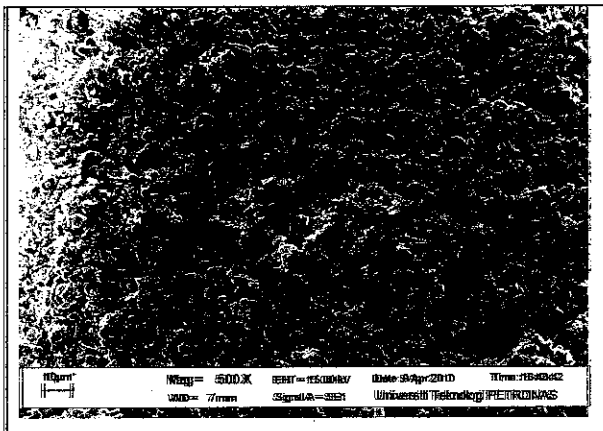


Figure 4.2 (a) : Top view of silica membrane for an hour dipping time

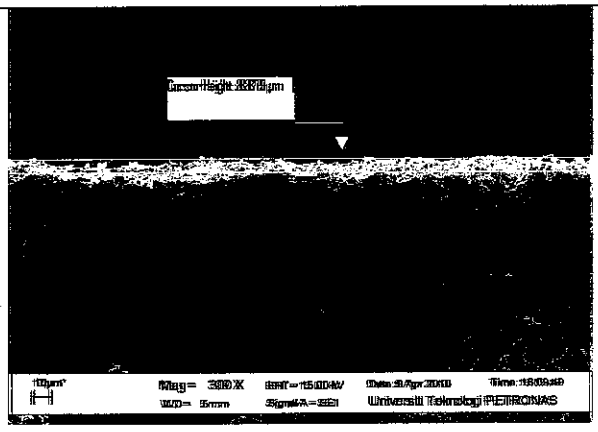


Figure 4.2 (b) : Cross section view of silica membrane for an hour dipping time

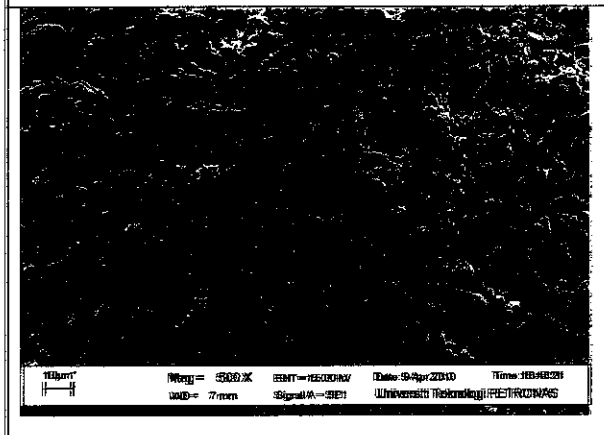


Figure 4.2 (c) : Top view of silica membrane for 2 hours dipping time

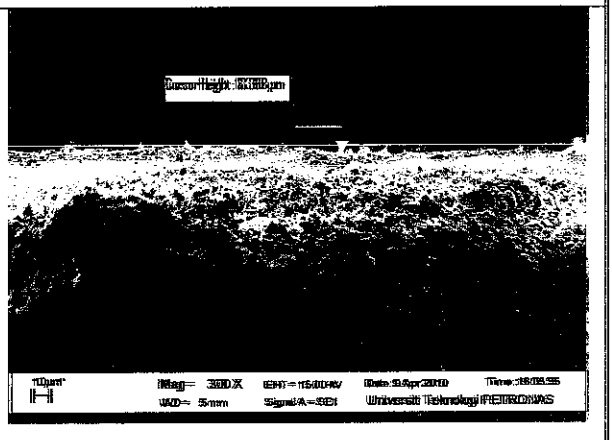


Figure 4.2 (d) : Cross section view of silica membrane for 2 hours dipping time

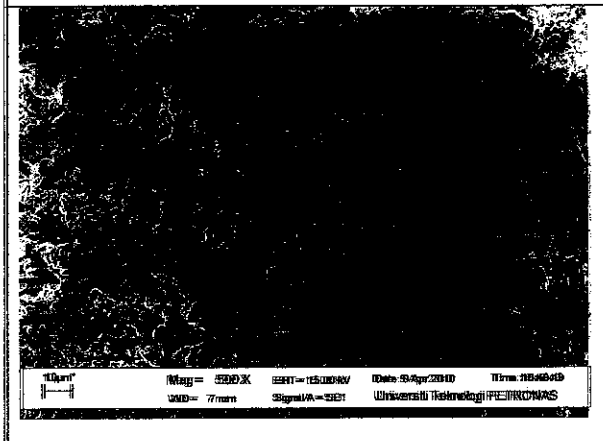


Figure 4.2 (e) : Top view of silica membrane for 3 hours dipping time

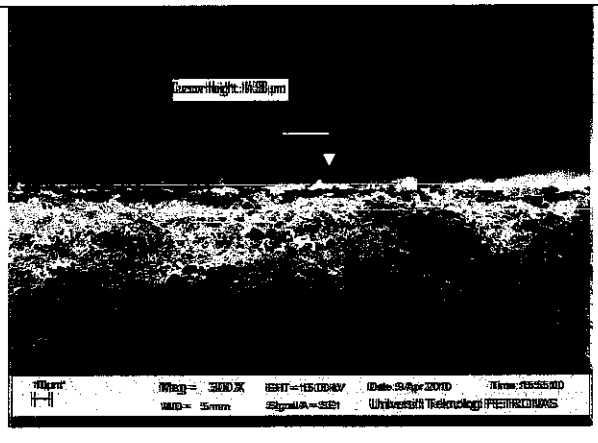


Figure 4.2 (f) : Cross section view of silica membrane for 3 hours dipping time

4.3 Gas Permeation Measurement

A permeation test through the samples was carried out using single component gas of carbon dioxide (CO2) and methane (CH4). In mesoporous membranes, at pressures below 10 bar ($1x10^5$ Pa), the permeation flux of a gas species is completely determined by Knudsen flow [9].

ıble 4.2 : Calculation for gas permeance : CO_2 permeance for dipping time of 1 hour

P bar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{[stp]}/cm^2.s$)	Nt (mol/s)	P ($mol/cm^2.s.Bar$)	P ($mol/m^2.s.Pa$)
.000	50.000	3.152	15.8629	14.6796	0.7476	0.001210	3.0815E-05	3.0815E-06
.500	50.000	2.796	17.8827	16.5486	0.8428	0.001710	3.4839E-05	3.4839E-06
.000	50.000	2.381	20.9996	19.4330	0.9897	0.002417	4.1034E-05	4.1034E-06
.500	50.000	2.044	24.4618	22.6370	1.1529	0.003294	4.7939E-05	4.7939E-06

ıble 4.3 : Calculation for gas permeance : CH_4 permeance for dipping time of 1 hour

P bar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{[stp]}/cm^2.s$)	Nt (mol/s)	P ($mol/cm^2.s.Bar$)	P ($mol/m^2.s.Pa$)
.000	50.000	3.674	13.6103	12.5950	0.6415	0.001031	2.6241E-05	2.6241E-06
.500	50.000	3.462	14.4442	13.3667	0.6808	0.001370	2.7900E-05	2.7900E-06
.000	50.000	3.063	16.3238	15.1060	0.7693	0.001860	3.1574E-05	3.1574E-06
.500	50.000	2.350	21.2766	19.6894	1.0028	0.002831	4.1190E-05	4.1190E-06

Table 4.4 : Gas Permeation Result for 1 hour dipping time

Pressure (kPa)	Typical Permeance Result, ($mol/m^2.s.Pa$)		Permselectivity
	Acid-Catalyst		Acid-Catalyst
	CO_2	CH_4	CO_2/CH_4
200	3.0815E-06	2.6241E-06	1.1743
250	3.4839E-06	2.7900E-06	1.2487
300	4.1034E-06	3.1574E-06	1.2996
350	4.7939E-06	4.1190E-06	1.3139

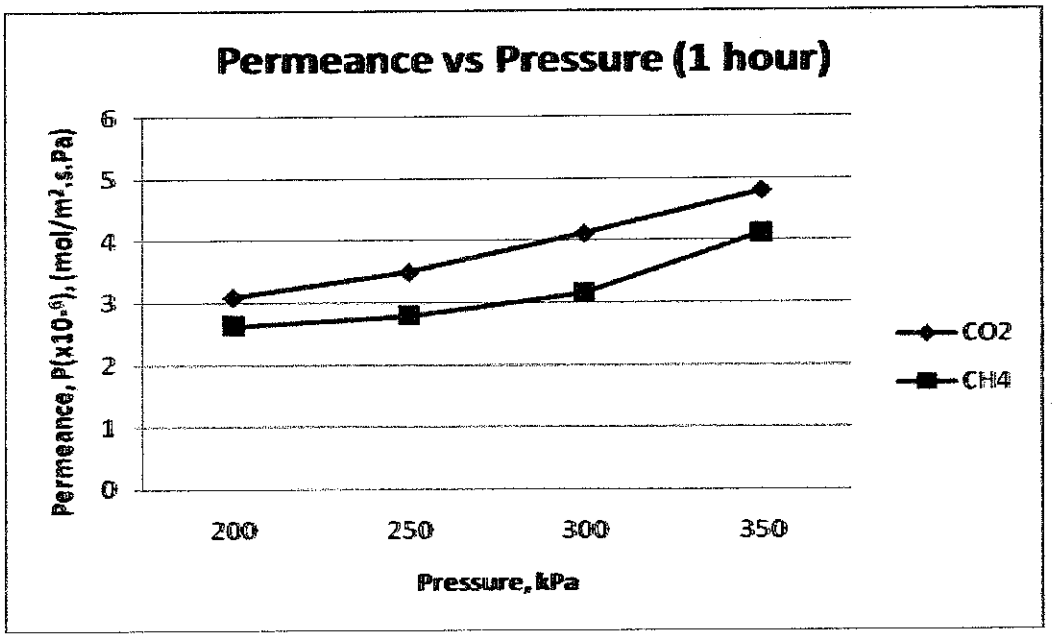


Figure 4.3 : CH_4 and CO_2 permeation versus pressure 1 hour of dipping time

ıble 4.5 : Calculation for gas permeance : CO_2 permeance for dipping time of 2 hours

P (bar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{[stp]}/cm^2.s$)	Nt (mol/s)	P (mol/cm^2.s.Bar)	P (mol/m^2.s.Pa)
.000	50.000	3.352	14.9165	13.8037	0.7030	0.001138	2.8977E-05	2.8977E-06
.500	50.000	2.996	16.6889	15.4439	0.7866	0.001596	3.2513E-05	3.2513E-06
.000	50.000	2.581	19.3723	17.9272	0.9130	0.002230	3.7854E-05	3.7854E-06
.500	50.000	2.244	22.2816	20.6194	1.0501	0.003001	4.3666E-05	4.3666E-06

ıble 4.6 : Calculation for gas permeance : CH_4 permeance for dipping time of 2 hours

P (bar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{[stp]}/cm^2.s$)	Nt (mol/s)	P (mol/cm^2.s.Bar)	P (mol/m^2.s.Pa)
.000	50.000	4.286	11.6671	10.7968	0.5499	0.000884	2.2506E-05	2.2506E-06
.500	50.000	3.957	12.6360	11.6934	0.5955	0.001199	2.4416E-05	2.4416E-06
.000	50.000	3.563	14.0332	12.9863	0.6614	0.001599	2.7147E-05	2.7147E-06
.500	50.000	3.168	15.7846	14.6071	0.7439	0.002100	3.0557E-05	3.0557E-06

Table 4.7 : Gas Permeation Result for 2 hours dipping time

Pressure (kPa)	Typical Permeance Result, (mol/m^2.s.Pa) Acid-Catalyst		Permselectivity Acid-Catalyst
	CO_2	CH_4	CO_2/CH_4
200	2.8977E-06	2.2506E-06	1.2875
250	3.2513E-06	2.4416E-06	1.3316
300	3.7854E-06	2.7147E-06	1.3944
350	4.3666E-06	3.0557E-06	1.4290

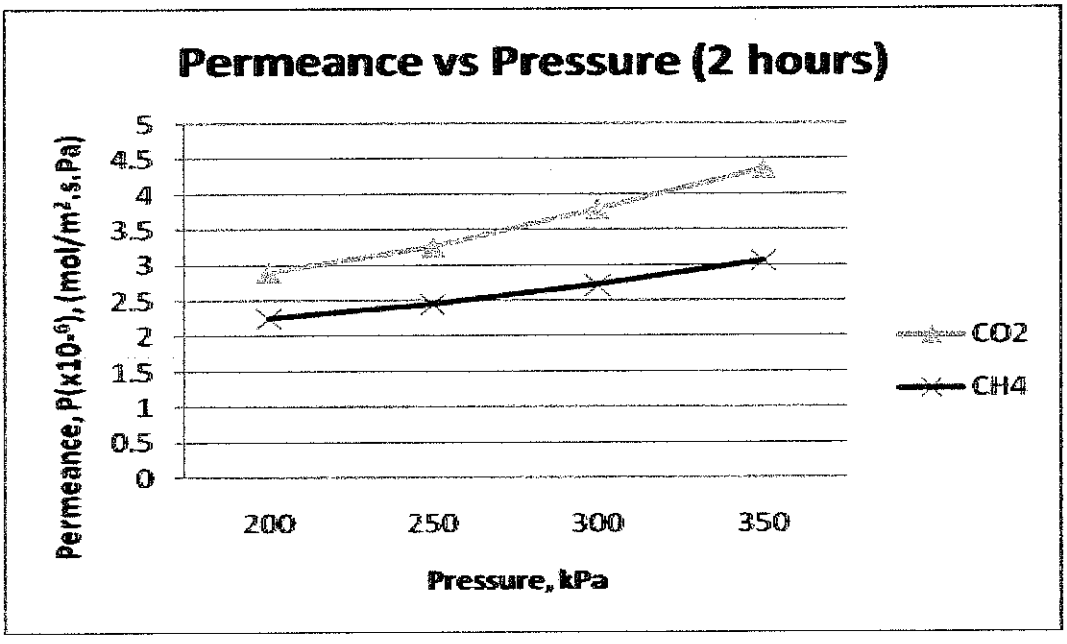


Figure 4.4 : CH_4 and CO_2 permeation versus pressure 2 hours of dipping time

Table 4.8 : Calculation for gas permeance : CO_2 permeance for dipping time of 3 hours

P (bar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{stp}/cm^2.s$)	Nt (mol/s)	P (mol/cm^2.s.Bar)	P (mol/m^2.s.Pa)
2.000	**50.000**	**3.552**	**14.0766**	**13.0265**	**0.6634**	**0.001074**	**2.7345E-05**	**2.7345E-06**
2.500	50.000	3.196	15.6446	14.4775	0.7373	0.001496	3.0478E-05	3.0478E-06
3.000	50.000	2.781	17.9791	16.6379	0.8474	0.002069	3.5132E-05	3.5132E-06
3.500	50.000	2.444	20.4583	18.9321	0.9642	0.002755	4.0093E-05	4.0093E-06

Table 4.9 : Calculation for gas permeance : CH_4 permeance for dipping time of 3 hours

P (lbar)	V (cm^3)	Time (s)	Q (cm^3/s)	Q_{stp} (cm^3/s)	J ($cm^3_{[stp]}/cm^2.s$)	Nt (mol/s)	P (mol/cm^2.s.Bar)	P (mol/m^2.s.Pa)
2.000	50.000	4.508	11.0902	10.2629	0.5227	0.0008401	2.1392E-05	2.1392E-06
2.500	50.000	4.308	11.6070	10.7411	0.5470	0.001101	2.2427E-05	2.2427E-06
3.000	**50.000**	**4.096**	**12.2068**	**11.2962**	**0.5753**	**0.001391**	**2.3613E-05**	**2.3613E-06**
3.500	50.000	3.758	13.3042	12.3117	0.6270	0.001770	2.5750E-05	2.5750E-06

Table 4.10 : Gas Permeation Result for 3 hours dipping time

Pressure (kPa)	Typical Permeance Result, (mol/m^2.s.Pa)		Permselectivity
	Acid-Catalyst		Acid-Catalyst
	CO_2	CH_4	CO_2/CH_4
200	2.7345E-06	2.1392E-06	1.2783
250	3.0478E-06	2.2427E-06	1.3590
300	**3.5132E-06**	**2.3613E-06**	**1.4878**
350	4.0093E-06	2.5750E-06	1.5570

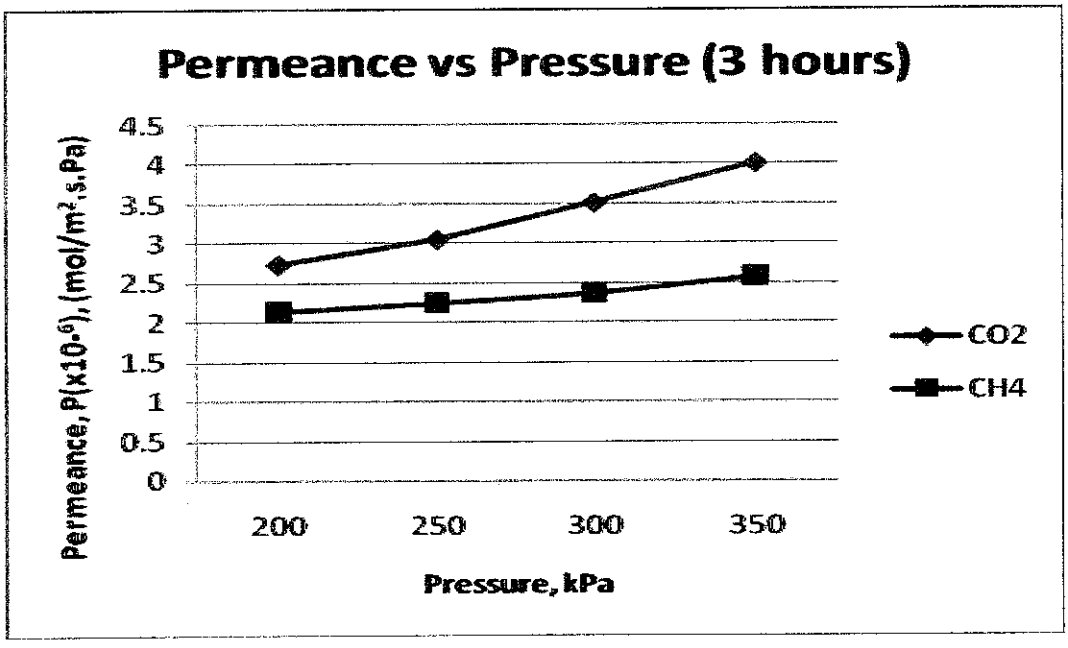


Figure 4.5 : CH_4 and CO_2 permeation versus pressure 3 hours of dipping time

From the results obtained, the permeance of the CO_2 is greater than CH_4 for all synthesized silica membrane, thus give the evidence that the mechanism of molecular differentiation by silica layer is through size selectivity. The highest permselectivity obtained by the silica membrane with 1 hour, 2 hours, and 3 hours dipping time are 1.3139, 1.4290, 1.5570 respectively. The result shows that the selectivity can be improved by controlling the dipping time so that optimal pore size and interconnected pore structure will be formed on the alumina porous support. Silica membranes with 3 hours dipping time results in good CO_2 permeance of 4.0093E-06 $mol/m^2.s.Pa$ with maximum permselectivity of **1.5570**.

The ideal Knudsen separation factor is the ratio of the square roots of the molecular weight of each species. The ideal Knudsen separation factor for CO_2 over CH_4 is 1.66 [25]. In this study, the maximum separation factor of 1.5570 is obtained at ΔP of 350 kPa for CO_2/CH_4 separation. Comparison between ideal Knudsen and experimental separation factor is slightly lower than ideal Knudsen. This small deviation from ideal Knudsen diffusion may be due to a minute number of microcracks produced on the membrane layer, which were not observable by SEM, but detected by this test. The defects of the coatings are also caused by a poor adhesion between the silica film and the alumina substrate [2]. Small defects and cracks often appear in thin films during the calcinations process. These defects can often be repaired by repeating the synthesis process.

The separation factor for CO_2/CH_4 obtained using synthesized silica membrane which is 1.3139 is smaller compared to other silica membrane produce by previous researcher. Ruldolph et al. managed to synthesize a high quality silica membrane that utilized nitric acid as a catalyst in hydrolysis process. All membrane produced have greater separation factor than the corresponding ideal Knudsen Diffusion separation factor especially for CO_2/CH_4. The separation factor for CO_2/CH_4 obtained by Ruldolph et al. was between 1.5-130 through their single and two step catalysed silica membranes.

The selectivity of the synthesized silica membrane can be improved through some modification which is by applying multiple separation layer of silica sol on the top or surface of the original silica coated membrane. This multiple separation layer can be done through sequences of dipping-drying-calcination step. In the other words, the membrane will be dipped in the silica sol, then dry before being calcined at desired calcinations temperature. Those steps will be repeated several times prior to get several separation layers on the membrane. It is found that, the selectivity of the membrane will be increased with an increase in the number of modified layer (M. Naito et. Al,1997). This can be explained by the self-repairing of the defect or microcracks existing in the previous formed separation layer of the silica membrane. This method of the formation of several separation layers will gradually decreased the pore size of the membrane leading to greater selectivity of separation gas especially CO_2 and CH_4 separation.

4.4 X-Ray Diffraction (XRD)

In order to study the structure of silica membranes on porous alumina support, the membrane in powder form is directly characterized by XRD. Figure 4.4 shows the XRD pattern of membranes (powder) calcined at 500°C for 3 hours. The sharp peaks in the range of wide-angle XRD correspond to the characteristic peaks of α-Al_2O_3. Those sharp diffraction peaks clearly indicated that the powders possess a periodic mesostructure.

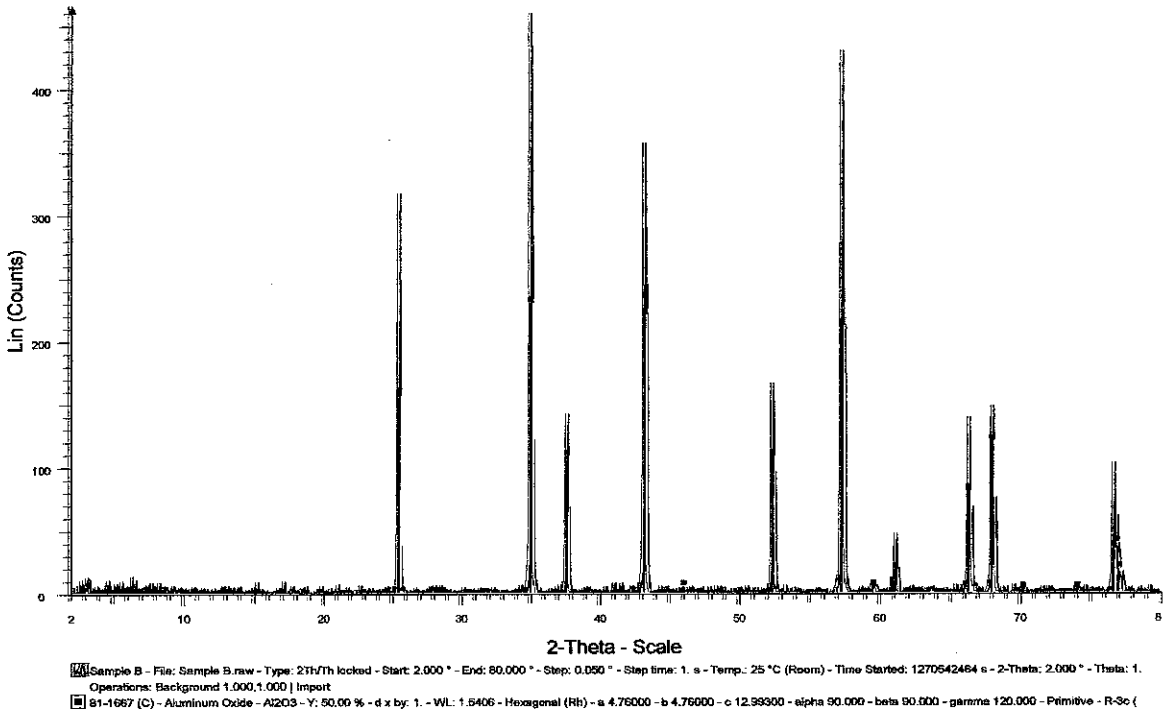


Figure 4.6 : XRD Pattern of samples calcined at 500°C

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

Results and findings from this project might be very useful in the industry. In this research, ceramic membrane is choosing as membrane due to its highly chemical, mechanical and thermal stability compared to polymeric membrane. Moreover, the cost of acid gases removal by using the mixed amines system is highly expensive. Due to that, we need to replace the amine adsorption with the most economical method and from this study, silica membrane is reasonable to be used as membrane for carbon dioxide removal since its pores size can be desirably controlled using sol-gel method involving particles.

Porous silica membranes were fabricated by the sol-gel procedures. Thin silica layers active for gas separation were formed on porous silica coated on α-alumina porous. The silica membranes managed to separate CO_2/CH_4 with a significant permeance value for both CO_2 and CH_4 (CO_2 permeance > CH_4 permeance) but with poor permselectivity of CO_2 over CH_4. This may due to the formation of microcracks or defect during calcination process. This selectivity can be improved through modification of the silica membrane by applying multiple separation layers on the porous alumina support by sequences of dipping-drying-calcination steps. The longer the dipping time, better pore size control and finer interconnected pore structure of silica layer on the alumina support.

As a conclusion, silica membrane is reasonable to be use as membrane for carbon dioxide removal since its pores size can be desirably controlled using sol gel method.

Recommendations:

There are few improvements to be recommended for the better experiment results in the next research:

i. **Using multilayer of silica thickness**

- The selectivity can be improved through modification of the silica membrane by applying multiple separation layers on the porous alumina support by sequences of dipping-drying-calcination step.

ii. **Dipping time of the membrane in Silica sol**

- The longer the dipping time, better pore size control and finer interconnected pore structure of silica layer on the porous alumina support

iii. **The pH condition of silica sol has an influence on both the microstructure of the membranes; the higher pH(9) can form crack-free membranes by filtration**

iv. **The chemical bonds between silica and the alumina can be easily obtained by subsequently heating these coated supports. The cracks that are often seen in silica membranes can be reduced or avoided.**

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APPENDIX

	Density,(kg/m^3)		Density,(g/cm^3)	
Pressure (Bar)	CO_2	CH_4	CO_2	CH_4
1	1.804	0.6552	0.001804	0.000655
1.5	2.713	0.984	0.002713	0.000984
2	3.628	1.313	0.003628	0.001313
2.5	4.548	1.644	0.004548	0.001644
3	5.474	1.975	0.005474	0.001975
3.5	6.405	2.306	0.006405	0.002306

Data :

- Area of alumina discs : 19.635 cm^2
- MW of CO_2 : 44.01
- MW of CH_4 : 16.04
- Ideal Knudsen Separation Factor, $\alpha = \frac{\sqrt{MW_{CO2}}}{\sqrt{MW_{CH4}}} = 1.66$
- The CO_2/CH_4 ideal selectivity (unitless), $\alpha_{CO2/CH4}$, of membrane can be determined by dividing CO_2 permeance $(P)_{CO2}$, over CH_4 permeance, $(P)_{CH4}$

$$\alpha_{CO2/CH4} = \frac{(P)_{CO2}}{(P)_{CH4}}$$